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IN RE APPLICATION OF: Laura ZANIBELLI, et al

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FOR: **PROCESS AND CATALYSTS FOR UPGRADING OF HYDROCARBONS  
BOILING IN THE NAPHTHA RANGE**

**REQUEST FOR PRIORITY UNDER 35 U.S.C. 119  
AND THE INTERNATIONAL CONVENTION**

Assistant Commissioner for Patents  
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Sir:

In the matter of the above-identified application for patent, notice is hereby given that the applicant claims as priority:

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Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Norman F. Oblon  
Attorney of Record  
Registration No. 24,618  
Surinder Sachar  
Registration No. 34,423



22850

(703) 413-3000  
Fax No. (703) 413-2220  
(OSMMN 1/97)



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Anmelder:  
Applicant(s):  
Demandeur(s):  
ENITECNOLOGIE S.p.A.  
20097 S. Donato Milanese (Milano)  
ITALY  
REPSOL PETROLEO S.A.  
28045 Madrid

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Further applicant(s) : ELF ANTAR FRANCE S.A.  
92400 COURBEVOIE  
FRANCE  
EURON S.p.A.  
20097 SAN DONATO MILANESE - MILAN  
ITALY  
AGIP PETROLI S.p.A.  
00198 ROME  
ITALY

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PROCESS AND CATALYSTS FOR UPGRADING OF HYDROCARBONS  
BOILING IN THE NAPHTHA RANGE

The present invention relates to the use of a catalytic system comprising a metal of group VIII, a  
5 metal of group VI, a metal oxide as carrier and suitable quantities of a component selected from a zeolite of the FER type, phosphorous, and a mixture thereof, in upgrading of hydrocarbons boiling in the naphtha range containing sulfur impurities, namely in  
10 hydrodesulfurization with contemporaneous skeleton isomerization of olefins contained in said hydrocarbons and/or with reduction of olefins hydrogenation, carried out in a single step.

This catalytic system can be used in particular for  
15 upgrading of hydrocarbons boiling in the naphtha range deriving from cracking processes, preferably of hydrocarbons boiling in the naphtha range derived from FCC (fluid catalytic cracking).

In fact hydrocarbons boiling in the naphtha range  
20 from FCC (i.e. gasoline cut ) are used as a component in the blending of reformulated gasolines. For this purpose, it must have a high octane number and also a low sulfur content, in compliance with the limits of the law, which are becoming more and more

hydrodesulfurization with a reduced octane loss, it is necessary to operate in two steps using specific catalysts and reactors.

US 5.378.352 describes a process in a single step  
5 for desulfurizing hydrocarbon fractions which boil within the range of gasolines by means of a catalyst comprising a metal of group VIII, a metal of group VI, a zeolite having a Constraint Index ranging from 1 to 12, and a metal oxide as a binder, at a process  
10 temperature which is preferably higher than 340°C. Suitable zeolites which can be used in this invention are the following: ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, MCM-22 and mordenite. The use of MCM-22 is indicated as being particularly preferred. In  
15 the example a catalyst containing MCM-22 in a high percentage with respect to the total weight of the catalyst (54 wt%) is used and the example relates to "heavy naphtha", a feed cut from FCC gasoline with a high S content, but poor in olefins and consequently  
20 not particularly subject to reduction in the octane number as a result of hydrogenation. The suitable process conditions are: temperature higher than 340 °C, pressure about 4 to 100 atm, LHSV 0.5 to 10h<sup>-1</sup>, ratio

conversion values, also at lower temperatures and pressures than those preferably used in the prior art, with contemporaneous skeleton isomerization of olefins and/or with very low extent of hydrogenation of  
5 olefins double bond, by means of a catalyst comprising a metal of group VIII, a metal of group VI, a metal oxide as carrier and suitable quantities of a component selected from a zeolite of the FER type, phosphorous and mixture thereof. The skeleton isomerization of  
10 olefins and/or the very low extent of hydrogenation of olefins double bond allow to obtain desulfurization of hydrocarbon boiling in the naphtha range with very low losses of RON ( research octane number) and MON (motor octane number).

15 These results are not only obtained in the desulfurization of hydrocarbon cuts which boil within the range of "heavy naphtha" (130° - 250°C), i.e. cuts poor in olefins, but also in the case of "full range naphtha" feeds which boil within the range of 35°-  
20 250°C, i.e. in the case of cuts rich in olefins.

A first object of the present invention therefore relates to a process for desulfurizing hydrocarbons

aqueous solution containing a soluble salt of the metal of group VI and  $H_3PO_4$ , or the catalyst is obtained by impregnation with an aqueous solution of  $H_3PO_4$  of a gel, dried and calcined, obtained mixing an alcohol  
5 dispersion containing a soluble salt of the metal of group VIII and an organic source of aluminum with an aqueous solution containing a soluble salt of the metal of group VI.

The weight percentage of phosphorous refers to contents  
10 expressed as elemental phosphorous; in the final catalyst phosphorous is in form of oxide.

When the catalyst contains a zeolite of the FER type, this zeolite is present in a much lower quantity than that contained in the catalysts used in US 5378352.  
15 Using this catalytic system characterized by a low content of FER zeolite, excellent desulfurization conversions are obtained, with contemporaneous skeleton isomerization of olefins, even at temperatures which are not high, at which there are lower losses of RON  
20 and MON than those caused by the same FER zeolites when used at quantities as high as those used in US 5378352



of group VIII, a metal of group VI, a metal oxide as carrier and a component A selected from a zeolite belonging to the FER type, in a quantity ranging from 5 to 30% by weight with respect to the total weight of the catalyst, and mixtures of said zeolite belonging to the FER type, in a quantity ranging from 5 to 30% by weight with respect to the total weight of the catalyst, with phosphorous in a quantity ranging from 0.1 to 10 % weight, preferably from 1 to 5 % wt, with respect to the total weight of the catalyst.

Preferably the catalysts used in the process of the present invention contain Cobalt and/or Nickel as metal of group VIII, whereas the metal of group VI is preferably selected from molybdenum and/or tungsten.

According to a particularly preferred aspect, Co and Mo are used. Preferably the weight percentage of metal of group VIII varies from 1 to 10% with respect to the total weight of the catalyst, more preferably from 2 to 6%, and the weight percentage of metal of group VI preferably varies from 4 to 20% with respect to the total weight of the catalyst, more preferably from 8 to 13. The weight percentages of metal of group VI and

A particularly preferred aspect of the present invention is that the zeolite ZSM-35 is used. This zeolite is described in US 4016245.

Preferably the zeolites are used in acid form, i.e. in  
5 the form in which their cation sites are prevalently occupied by hydrogen ions and a particulalry preferred aspect is that at least 80% of the cation sites is occupied by hydrogen ions. Preferably the zeolites in acid form have Si/Al ratio < 20.

10 The catalyst used in the present invention containing zeolite FER as component A, preferably ZSM-35, can be prepared according to the traditional methods. For example by mixing the zeolite with the metal oxide followed by extrusion, calcination, a  
15 possible exchange process which reduces the sodium content, drying, impregnation with a solution containing a salt of a metal of group VI, drying, calcination and impregnation with a solution of a salt of a metal of group VIII, drying and calcination.

20 A particularly preferred aspect of the process of the present invention is to use a catalyst containing

preferred aspect is to operate in the presence of formamide (Drying Control Chemical Agent) which favours the stabilization of the porous structure during the drying phase.

5 The quantities of the reagents are selected in relation to the composition of the final catalyst.

In step c), according to the preferred sequence, the solution from step b) is added to the suspension of step a).

10 In step d) the so obtained gel is maintained at a temperature from 10° to 40°C, for a time ranging from 15 to 25 h.

Step e) is carried out at a temperature ranging from 80 to 120°C.

15 Step f) is carried out at a temperature ranging from 400 to 600°C.

The catalysts containing zeolite of FER type, as component A, prepared according to the sol-gel method, are new, show the lowest losses of RON and MON  
20 comparated with the catalysts having the same composition prepared according to the known techniques and are a further aspect of the present invention.

sieved in particles of  $<0.2$  mm and then, in step c), mixed with the zeolite by physical mixture or by dispersing the particles in an organic solvent such as cyclohexane or cyclohexanol. The solvent is vaporized  
5 and the catalyst particles dried and calcined. The mixing of step c) can be also carried out by mixing and homogenizing a solid mixture comprising the impregnated metal oxide ( of particle size  $< 0.2$  mm ), the zeolite, a binder and optionally combustible organic polymers.  
10 The mixture so obtained can be kneaded with a peptizing acid solution, extruded, dried and calcined by any conventional method. Alternatively, the paste can be pelletized, dried and calcined by any conventional method.  
15 When a catalyst containing both zeolite and phosphorous is used in the process of the present invention, it can be prepared using the above mixing procedure where in the step a) the metal oxide carrier is first impregnated with an aqueous solution of  $H_3PO_4$  and then  
20 is impregnated with an aqueous solution of metal of group VIII and an aqueous solution of metal of group VI.

3) by impregnation with an aqueous solution of  $H_3PO_4$  of a gel, dried and calcined, obtained mixing an alcohol dispersion containing a soluble salt of the metal of group VIII and an organic source of aluminum with an aqueous solution containing a soluble salt of the metal of group VI.

In the first preparation the impregnations are carried out with any conventional method. Preferably the metal oxide carrier has a surface area lower than  $240 \text{ m}^2/\text{g}$ .  
Between the impregnation with phosphoric acid and the impregnation with the metals drying and calcination are carried out.

In the second and third preparations, the conditions and quantities of sol-gel technique are used, as those above described in the sol-gel preparation of the catalyst containing zeolite FER as component A.

The catalysts used in the process of the present invention only containing phosphorous as component A, from 0.1 to 10 % wt, obtained with one of the above three methods, are new and are another aspect of the present invention.

hydrodesulfurization according to the process of the present invention consists of hydrocarbons boiling in the naphtha range deriving from cracking or coking processes. In the following examples catalysts  
5 preparations are reported, and upgrading tests either on a model feed or on a full range FCC naphtha.

#### EXAMPLE 1

In this example a catalyst containing Co, Mo, alumina and ZSM-35 is prepared by sol-gel procedure.

10 0.88 g. of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  are dissolved in 33.55 grams of butanol, at room temperature, in a beaker, under stirring. 0.99 g. of ZSM-35 ( prepared according to US 4016245), in acidic form, having the following characteristics:  $(\text{Si}/\text{Al})_{\text{mol}} = 13.8$ ;  $\text{Na}(\text{g}/\text{Kg zeolite}) =$   
15 0.1; Surface area =  $490 \text{ m}^2/\text{g}$ ; Pore volume =  $0.235 \text{ cm}^3/\text{g}$ , are dispersed in this alcohol solution. 28.17 g. of aluminum sec-butoxide  $\text{Al}(\text{C}_4\text{H}_9\text{O})_3$  are added to the suspension thus obtained, heating for 15 minutes under stirring, to  $80^\circ\text{C}$ . A second solution is prepared by  
20 dissolving 1.28 g. of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 8.86 g. of distilled water, at room temperature, under stirring,

thus obtained, heating for 15 minutes under stirring,  
to 80°C.

A second solution is prepared by dissolving 1.54  
g. of  $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in 8.33 g. of distilled water, at  
5 room temperature, under stirring, for about 5 minutes;  
1.35 g. of formamide are then added and the mixture is  
heated to 80°C for 5 minutes. Then the catalyst is  
treated as in the Ex.1.

The composition and characteristics of the obtained  
10 catalyst are indicated in Table 1.

### EXAMPLE 3

In this example a catalyst containing Co, Mo, alumina  
and ZSM-35 is prepared by sol-gel procedure.

1.11 g. of  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  are dissolved in 31.05  
15 grams of butanol, at room temperature, in a beaker,  
under stirring. 3 g. of ZSM-35, having the same  
characteristics as in previous examples, are dispersed  
in this alcohol solution.

26.835 g of aluminum sec-butoxide  $\text{Al}(\text{C}_4\text{H}_9\text{O})_3$  are  
20 added to the suspension thus obtained, heating for 15  
minutes under stirring to 80°C.

hydrotreating catalysts, is prepared by a typical procedure of impregnation of  $\gamma$ -Alumina support.

227 grams of pseudoboehmite (Versal 250, LaRoche Chemicals) are mixed with 15 grams of  
5 microcristalline cellulose (Avicel, PH-101). This mixture of solids is kneaded for one hour with an acid solution prepared by solving 12,5 grams of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 247,14 grams of distilled water. The  
resulting paste is extruded and the extrudates are  
10 dried at room temperature and then calcined at 700 °C for 4 hours.

Previous to impregnation the extrudates are crushed and sieved up to a particle size of 0,2-0,3 mm. 10,46 grams of this support are impregnated with 15 ml of a  
15 solution of Amonium heptamolibdate (AHM) plus 2,5 ml of distilled water. The AHM solution is prepared by solving 13,8 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in distilled water, adjusting the pH to 7 (aprox.) with  $\text{NH}_4\text{OH}$  and adding water up to 50 ml. The impregnation is done at room  
20 temperature for one hour. Then the sample is vacuum dried for one hour at 60 °C and calcined at 300°C for 2 hours. 13,12 grams of this sample are impregnated with 7,7 ml of a Cobalt solution plus 10,7 ml of



impregnated in excess. 100 ml of impregnating solution contains 7,5 g of  $H_3PO_4$  (85%) and distilled water. The product is filtered and dried at 120 °C overnight, and then calcined at 700 °C for four hours.

5 4,35 grams of the P impregnated support are impregnated with 6 ml of a AHM solution plus 1,3 ml of distilled water for one hour. The AHM solution is prepared by solving 27,6 g of  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  in distilled water, adjusting the pH to 7 (aprox.) with  
10  $NH_4OH$  and adding water up to 100 ml. The impregnation is done at room temperature for one hour. Then the sample is vacuum dried for one hour at 60 °C and calcined at 300°C for 2 hours. 5,69 grams of this sample are impregnated with 5,3 ml of a Cobalt  
15 solution plus 2,7 ml of water for one hour. 50 ml of Cobalt solution are prepared by solving 11 g of  $Co(NO_3)_2 \cdot 6H_2O$  in distilled water. The impregnation is done at room temperature for one hour. Then, the sample is vacuum dried for one hour at 60 C° and  
20 calcined at 500 °C for 4 hours.

EXAMPLE 8

In this example a catalyst containing Co, Mo, alumina and ZSM-35 is prepared by impregnation technique.

139,24 grams of pseudoboehmite (Versal 250, LaRoche  
5 Chemicals) are mixed with 13,73 grams of ZSM-35 of  
ex.1, and 13,92 grams of hydroxyethyl-cellulose (HEC  
15000H, BP). This mixture of solids is kneaded for  
one hour with 183,1 grams of an acid solution  
prepared by solving 2,66 grams of  $\text{HNO}_3$  (62,7%) in  
10 180,44 grams of distilled water. The resulting paste  
is extruded and the extrudates are dried at room  
temperature and then calcined at 600 °C for 4 hours.

Previous to impregnation the extrudates are crushed  
and sieved up to a particle size of 0,2-0,3 mm. 9,18  
15 grams of this support are impregnated with 8,4 ml of  
a solution of AHM plus 7 ml of distilled water. The  
AHM solution is prepared by solving 21,68 g of  
( $\text{NH}_4$ )<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O in distilled water, adjusting the pH  
to 7 (aprox.) with  $\text{NH}_4\text{OH}$  and adding distilled water up  
20 to 100 ml. The impregnation is done at room  
temperature for one hour. Then the sample is vacuum  
dried for one hour at 60 °C and calcined at 300°C for  
2 hours. 10,32 grams of this sample are impregnated

12,66 grams of  $\gamma$ -Alumina support, prepared as described in EXAMPLE 5, are impregnated with 21 ml of AHM solution, prepared by solving 35,1 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in distilled water, adjusting the pH to 7 (aprox.) with  $\text{NH}_4\text{OH}$  and adding distilled water up to 100 ml. The impregnation is done at room temperature for one hour. Then the sample is vacuum dried for one hour at 60 °C and calcined at 300°C for 2 hours. 16,9 grams of this sample are impregnated with 23,6 ml of a Cobalt solution. 50 ml of Cobalt solution were prepared by solving 10 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in distilled water. The impregnation is done at room temperature for one hour. Then, the sample is vacuum dried for one hour at 60 C° and calcined at 500 °C for 4 hours. The physical mixture of this catalyst and ZSM-35 of ex.1 is carried out as shown in EXAMPLE 9.

The composition and characteristics of the obtained catalyst are reported in Table 1.

#### 20 EXAMPLE 11

This Example is to show the preparation of a catalyst containing Co, Mo,  $\gamma\text{-Al}_2\text{O}_3$ , phosphorous and ZSM-35. The catalyst is prepared by mixing an already

Table 1

	1	2	3	4	5 (\$)	6 (\$\$)	7 a)	b)	c)	8	9	10	11
Co (wt%)	2.3	6	2.2	2.1	3,78	3,5	3,8	3.8	4	2,32	3,42	3,47	3,21
Mo (wt%)	8.6	9.9	8.6	7.8	15,3	12,8	13,6	13.9	15	8,93	13,8	13,2	11,2
Co/Mo	0.45	1	0.43	0.45	0,40	0,44	0,45	0.45	0.45	0,42	0,40	0,43	0,47
Zeol. (wt%)	10.1	7.95	29.55	29.6	-	-	-	-	-	10	10	30	10
Al2O3 wt%	71.8	67.85	56.1	55	72,2	69,8	69,4	69	65	73,6	64,9	45,7	61,9
P (wt%)	---	---	---	2.4	-	2,84	3,5	3.7	2.5	-	-	-	3,13
Surf. area (m2/g)	315	300	460	310	171	156	137	150	186	281	171	148	137
Pore Vol. (cm3/g)	0.92	0.78	1.11	0.85	0,64	0,44	0,51	0.51	0.57	0,64	0,64	0,59	0,51
						(!)				(!)	(!)	(!)	(!)

(\$): Comparative catalyst ; (\$\$) Comparative commercial catalyst. Also tested with full range FCC naphtha; (!)

values are of extrudates ; (!!) values are of catalyst before mixing with zeolite

aging for 21 hours in a beaker at room temperature, the product is dried on a heating plate, under a stream of  $N_2$ .

60 grams of the catalyst thus dried are mixed with  
5 40 grams of an aqueous solution of acetic acid (4%), kneaded and extruded. The extruded product is dried for a night in a vacuum oven at 100°C and is calcined in a muffle furnace up to 550°C for 3 hours. The composition and characteristics of the extruded catalyst is  
10 reported in Table 2.

EXAMPLE 13 ( comparative)

A catalyst is prepared following the same procedure as described in patent US 5378352. The zeolite used is ZSM-35 of ex.12 instead of MCM-22 employed in the  
15 mentioned patent.

43,93 grams of pseudoboehmite (Versal 250, LaRoche Chemicals) are mixed with 109,52g of ZSM-35 and 14 grams of hydroxyethyl cellulose (HEC 15000H , BP). The solid is kneaded with an acid solution obtained  
20 by solving 0,841 grams of  $HNO_3$  (62,7%) in 181,69 grams of distilled water. The paste so formed is extruded. These extrudates are dried at room temperature and calcined at 600 °C during 4 hours.

excess with a solution that contains 75 grams of  $H_3PO_4$  (85%) per litre of aqueous solution. The extrudates are then drained, dried in air and calcined at  $700^\circ C$  for 4 hours. Then the extrudates are impregnated in excess first with AHM and then with Cobalt nitrate as shown in EXAMPLE 13. Drying and calcination method are also as in EXAMPLE 13. The composition and characteristics of the catalysts are reported in Table 2.

#### EXAMPLE 16

A  $\gamma$ -Alumina support is prepared as described in EXAMPLE 5. The support is crushed and sieved at a particle diameter  $<0,2mm$ . This support is impregnated as shown in EXAMPLE 5 . 9,31 grams of this CoMo/ $\gamma$ - $Al_2O_3$  catalyst are mixed with 3,86 grams of ZSM-35 of ex 12, 1,243 grams of hydroxyethyl cellulose (HEC 15000H, BP Chemicals)) and 8,87 grams of pseudoboehmite V700 (LaRoche Chemicals). This mixture is kneaded with an acid solution that contains 0,54 grams of  $HNO_3$  (62,7%) in 21,96 grams of distilled water. The resulting paste is extruded and the extrudates are dried at room temperature and calcined at  $500^\circ C$  during 4 hours. The composition and

Table 2

EXAMPLE	12	13 (\$)	14	15	16	17
Co (wt%)	2,2	3,08	2,8	3,47	1,87	1,77
Mo (wt%)	8,9	7,93	9,3	6,97	7,08	6,7
Co/Mo	0,41	0,63	0,49	0,81	0,43	0,43
Zeol. (wt%)	10	55	9,82	-	19,84	20,37
Al <sub>2</sub> O <sub>3</sub> wt%)	72	29,04	72,67	77,84	67,16	63,47
P (wt%)	-	-	-	3,18	-	1,66
Surf. Area m <sup>2</sup> /g	315	303	281	157	302	270
Pore Vol (cm <sup>3</sup> /g)	0,63	0,56 **	0,46 **	0,61 **	0,75 **	0,67 **

(\$): Comparative catalyst ; (\*\*): Hg

EXAMPLE 18 ( test on model feed )

10            1 g of the catalyst of EXAMPLE 1 is charged in a reactor and activated in the presence of H<sub>2</sub>S (10% vol in H<sub>2</sub> ) up to 400°C. A mixture, representative of olefinic naphtha composition, is then fed consisting of thiophene (corresponding to 1000 ppm of S), 1-pentene (30%w) and the rest n-hexane at WHSV = 5 h<sup>-1</sup>,  
 15            P<sub>tot</sub> = 10 bars and H<sub>2</sub>/HC ratio 100 (stdl/l).

The temperature varies from 200 to 300 °C. At each temperature the full product composition is analyzed by gas chromatography. Table 3 indicates the conversion values in HDS and the conversion in ISO %,
 37.

3. This catalyst shows higher catalytic activity with respect to the catalyst of EXAMPLE 1.

#### EXAMPLE 21

1 gram of the catalyst of EXAMPLE 4 is treated as in EXAMPLE 18 and is then subjected to HDS reaction as in the above example. The results are reported in Table 3. The presence of P and ZSM-35 decreases the olefin hydrogenation while maintaining olefin isomerization.

#### EXAMPLE 22 (comparative)

1g of catalyst of EXAMPLE 5 was tested in a continuous flow standard hydrodesulfurization reactor as in EXAMPLE 18, except that LHSV was  $5\text{h}^{-1}$  and the ratio hydrogen /hydrocarbon was 300 Nl/l. The results are reported in Table 3. The isomerization activity of such catalyst is very low.

#### EXAMPLE 23 (comparative)

1 gram of the catalyst of EXAMPLE 6 is charged in the reactor and activated as described in EXAMPLE 22. Then, it is used in the reaction trials following the procedure of EXAMPLE 22. The results are reported in Table 3. This commercial catalyst shows a similar hydrogenation and isomerization activity than the comparative catalyst of EXAMPLE 22. Consequently,



procedure of Example 22. The results are reported in Table 3. The extent of isomerization is increased when ZSM-35 is included in the support and the catalyst is then prepared by impregnation, as described in Example 8 in respect to the comparative catalysts of Ex. 5 and 6, even if the isomerization is lower than in case of catalyst prepared by sol-gel, with the same composition ( Ex.1) .

#### EXAMPLE 26

1 gram of the catalyst of Example 9 is charged in the reactor and activated as described in Example 22. Then, it is used in the reaction trials following the procedure of Example 22. The results are reported in Table 3. If ZSM-35 is included in the catalyst formulation by mechanical mixing, as described in Example 9, increases the isomerization activity in respect to the catalyst of Ex. 8.

#### EXAMPLE 27

1 gram of the catalyst of Example 10 is charged in the reactor and activated as described in Example 22. Then, it is used in the reaction trials following the procedure of Example 22. The results are reported in Table 3. The increase in ZSM-35 content, when the catalyst is produced according to Example 10 produces

Table 3

EXAMPLE	CATALYST	TEMP., °C	HDS, %	HYD, %	ISO, %
18	Ex.1	250	43	29	35
		280	81.6	57.9	64.1
19	Ex.2	250	51.4	27.5	22.6
		280	90.6	66.2	58.12
20	Ex.3	250	81.4	47.6	64.3
		280	99.3	92.9	63.7
21	Ex.4	250	79.5	32.3	33.6
		280	98.5	79.5	54.2
22	Ex. 5	250	90.9	45.3	3.96
		280	100	97.6	2.33
23	Ex 6	240	91.60	43.83	2.95
		260	100.00	86.16	3.26
24	Ex. 7 case a	250	95.84	30.62	3.13
		280	100	74.84	3.89
	case b	225	73.51	28.48	3.24
		250	98.93	81.98	4.52
	case c	225	87.52	41.06	2.82
		250	100	90.22	3.10
25	Ex. 8	240	87.82	52.15	6.25
		250	98.94	72.52	10.59
		280	100	99.22	23.76
26	Ex. 9	245	67.13	31.10	22.69
		270	100.00	65.00	54.95
27	Ex. 10	230	24.80	7.22	48.79
		260	85.04	23.21	77.97
		270	93.97	36.68	77.06
28	Ex. 11	260	71.94	16.8	66.08
		270	92.62	24.37	72.00

### 15 Examples of upgrading of full range FCC naphtha

In the following series of experiments catalysts of EXAMPLES 12 to 17 are tested in a continuous flow reactor for desulfurization of full range FCC naphtha. Also, the reference commercial catalyst of EXAMPLE 6 is tested. The composition of full range FCC naphtha is reported in Table 4.

EXAMPLE 29 (comparative)

In this comparative example 25 cm<sup>3</sup> of catalyst of Example 6 are placed in the reactor. The catalyst is treated in air increasing the temperature at 5 °C/min up to 400 °C, and it is maintained at this temperature for 2 hours. The catalyst is brought to room temperature overnight. Then a flow of 0,450 Nl/min of a mixture of 95% H<sub>2</sub> and 5% H<sub>2</sub>S is passed through the reactor. The temperature is increased up to 320 °C at 3 °C/min, and this temperature is maintained for two hours. Then the temperature is increased up to 400 °C at 2 °C/min and it is maintained for one hour. Then the reactor temperature is set at 360 °C overnight. The conditions used for the desulfurization process are:

Hydrogen pressure : 10 kg/cm<sup>2</sup> , Liquid space velocity: 4 h<sup>-1</sup> ; Hydrogen/Hydrocarbon ratio: 400 Nl/l ;

Temperature: 260-300 °C

Table 5 shows the results of the tests.

Table 6. Results Example 30

Catalyst Example 13		FEED			
<b>CONDITIONS</b>					
Temperature, °C			350	340	330
Pressure, kg/cm <sup>2</sup>			40	40	40
LHSV, h <sup>-1</sup>			1	1	1
Ratio H <sub>2</sub> /HC, N/I			200	200	200
<b>PRODUCT CHARACTERISTICS</b>					
Sulfur, ppm	ASTM D-5453	2390	42	100	170
Bromine No	ASTM D-1159	55,6	1,72	0,7	2,1
Analisis PIONA (%wt):					
naphthenes	8,11		13,1	13,3	13,0
i-paraffins	24,53		38,8	40,2	39,6
n-paraffins	3,64		10,5	11,0	11,1
cycl-olefines	2,95		0,1	0,1	0,1
i-olefines	13,94		0,6	0,0	0,2
n-olefines	8,66		0,1	0,0	0,0
aromatics	30,23		28,7	28,0	28,0
>200°C	7,91		8,1	7,5	7,9
RON	ASTM D-2699	91,4	78	78	78,5
MON	ASTM D-2700	80,5	75,2	75,1	75,3

The octane losses obtained are very high in all the range of temperatures tested. RON loss is in the order of 13 units and MON loss is in the order of 5 to 6 units.

EXAMPLE 31

In this example 25 cm<sup>3</sup> of catalyst of Example 14 is placed in the reactor. The catalyst is activated following the procedure shown in Example 29. Then the desulfurization of full range FCC naphtha is carried out as described in Example 29. Table 7 shows the results of the tests.

Table 8. Results Example 32

catalyst Example 15		FEED			
CONDITIONS					
Temperature, °C			310	310	320
Pressure, kg/cm2			10	10	10
LHSV, h-1			4	1,5	1,5
Ratio H2/HC, N/I			400	400	400
PRODUCT CHARACTERISTICS					
Sulfur, ppm	ASTM D-5453	2209	295	241	63
Bromine No	ASTM D-1159	54,6	42,24	29,1	24,6
Analisis PIONA (%wt):					
naphtenes	8,11			10,2	10,7
i-paraffins	24,53			30,7	32,9
n-paraffins	3,64			6,6	7,4
cycl- olefines	2,95			1,7	1,1
i-olefines	13,94			8,7	7,1
n-olefines	8,66			3,9	3,2
aromatics	30,23			30,4	29,8
>200°C	7,91			7,9	7,7
RON	ASTM D-2699	91,4	90,2	86,3	85,7
MON	ASTM D-2700	80,5	80,2	79,0	78,8

10 Octane losses are lower than with both comparative catalysts tested in 29 and 30, confirming the results obtained with synthetic feed. At very low S content the extent of hydrogenation of olefines is lower than the other catalysts.

#### 15 EXAMPLE 33

In this example 25 cm<sup>3</sup> of catalyst of Example 16 is placed in the reactor. The catalyst is activated following the procedure shown in Example 29. Then the desulfurization of full range FCC naphtha is carried out as described in Example 29. Table 9 shows the results of the tests.

Table 10

CATALYST EXAMPLE 17		FEED				
<b>CONDITIONS</b>						
Temperature, °C			320	312	304	296
Pressure, kg/cm <sup>2</sup>			10	10	10	10
LHSV, h <sup>-1</sup>			1.5	1.5	1.5	1.5
Ratio H <sub>2</sub> /HC, NI/I			400	400	400	400
<b>PRODUCT CHARACTERISTICS</b>	<b>STANDARD</b>					
Sulfur, ppm	ASTM D-5453	2209	63	130	204	230
Bromine No	ASTM D-1159	54.6	18.1	28.3	35.3	38.5
Analysis PIONA (%wt):						
naphtenes	8.11		10.84	10.2		
i-paraffins	24.53		33.97	29.2		
n-paraffins	3.64		7.94	6.5		
cycl- olefines	2.95		0.89	1.7		
i-olefines	13.94		5.54	8.4		
n-olefines	8.66		2.08	3.5		
aromatics	30.23		30.86	31.6		
>200°C	7.91		7.82	9.0		
RON	ASTM D-2699	91.4	84.0	86.8	88.4	88.9
MON	ASTM D-2700	80.5	78.2	78.9	79.5	79.6

Octane losses are lower than with both comparative catalysts tested in Ex. 29 and 30, confirming the results obtained with synthetic feed.

#### EXAMPLE 35

In this example 25 cm<sup>3</sup> of catalyst of Example 12 is placed in the reactor. The catalyst is activated following the procedure shown in Example 29. Then the desulfurization of full range FCC naphtha is carried out as described in Example 29. Table 11 shows the results of the tests.

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## CLAIMS

- 1) Process for desulfurizing hydrocarbons which boil within the range of 35° to 250°C, containing olefins and more than 150 ppm of sulfur , with possible skeleton isomerization of olefins, using a catalyst which comprises a metal of group VIII, a metal of group VI, a metal oxide as carrier and a component A selected from:
- a) zeolite belonging to the FER type, in a quantity ranging from 5 to 30% by weight with respect to the total weight of the catalyst,
- b) phosphorous in a quantity ranging from 0.1 to 10 % weight with respect to the total weight of the catalyst,
- c) mixtures thereof,
- where when the component A is only phosphorous either the catalyst is obtained by impregnation of the metal oxide carrier with an aqueous solution of  $H_3PO_4$  followed by impregnation with an aqueous solution of the metal of group VIII and an aqueous solution of the metal of group VI, or the catalyst is obtained by drying and calcination of a gel obtained mixing an alcohol

from 0.1 to 10 % weight with respect to the total weight of the catalyst.

3) The process according to claim 1 or 2 wherein the metal of group VIII is selected from Cobalt, Nickel and their mixtures.

4) The process according to claim 1 or 2 wherein the metal of group VI is selected from molybdenum, tungsten and their mixtures.

5) The process according to claims 3 and 4 wherein the metal of group VIII is cobalt and the metal of group VI is molybdenum.

6) The process according to claim 1 or 2 wherein the weight percentage of metal of group VIII varies from 1 to 10% with respect to the total weight of the catalyst.

7) The process according to claim 6 wherein the weight percentage of metal of group VIII varies from 2 to 6%.

8) The process according to claim 1 or 2 wherein the weight percentage of metal of group VI varies from 4 to 20% with respect to the total weight of the catalyst.

9) The process according to claim 8 wherein the weight percentage of metal of group VI varies from 8 to 13 %.



17) The process according to claim 16, wherein at least 80% of the cation sites is occupied by hydrogen ions.

18) The process according to claim 1, 2, 14 or 15, wherein the zeolite has Si/Al ratio  $< 20$ .

5 19) The process according to claim 1 or 2 wherein the catalyst contains zeolite of FER type as component A, and is prepared as follows:

10 a) an alcohol dispersion is prepared, containing a soluble salt of the metal of group VIII, the zeolite of the FER type and an organic source of aluminum;

b) an aqueous solution is prepared, containing a soluble salt of the metal of group VI and optionally formamide;

15 c) the alcohol dispersion and the aqueous solution are mixed, obtaining a gel;

d) aging of the gel at a temperature ranging from 10 to 40°C;

e) drying of the gel;

f) calcination of the gel.

20 20) The process according to claim 19, wherein in step

a) the metal salt of group VIII is nitrate.

c) mixing the impregnated metal oxide obtained from step b) with the zeolite of FER type.

26) The process according to claim 25 wherein the impregnated metal oxide from step b) is crushed and  
5 sieved in particles of  $<0.2$  mm before the mixing in step c).

27) The process according to claim 26 wherein in the step c) metal oxide particles and zeolite of FER type are dispersed in an organic solvent, then the solvent  
10 is vaporized and the so obtained catalyst is dried and calcined.

28) The process according to claim 26 wherein in step c) metal oxide particles and zeolite of FER type are mixed in the presence of a binder and optionally of a  
15 combustible organic polymer, to obtain a mixture which is kneaded with a peptizing acid solution, extruded, dried and calcined, or pelletized, dried and calcined.

29) The process according to claim 1 or 2 wherein the catalyst contains phosphorous in a quantity ranging  
20 from 1 to 5 % wt with respect to the total weight of the catalyst.

b) an aqueous solution is prepared, containing a soluble salt of the metal of group VI and optionally formamide;

c) the alcohol dispersion and the aqueous solution are mixed, obtaining a gel;

d) aging of the gel at a temperature ranging from 10 to 40°C;

e) drying of the gel;

f) calcination of the gel.

33) A catalyst which comprise a metal of group VIII, a metal of group VI, a metal oxide as carrier, a zeolite of the FER type, in a quantity ranging from 5 to 30% by weight with respect to the total weight of the catalyst, and phosphorous in a quantity ranging from 0.1 to 10%.

34) A process for preparing the catalyst of claim 33 comprising the following steps:

a) an alcohol dispersion is prepared, containing a soluble salt of the metal of group VIII, the zeolite of FER type and an organic source of aluminum;

f) calcination of the gel.

g) impregnation of the catalyst obtained from step f) with an aqueous solution of  $H_3PO_4$ , drying and calcination.

5 36) Process for preparing the catalyst of claim 33 comprising:

- a) impregnation of metal oxide with an aqueous solution of  $H_3PO_4$ , drying and calcination,
- 10 b) impregnation of the material resulting from step a) with an aqueous solution of metal of group VIII and an aqueous solution of metal of group VI,
- c) drying and calcination of the material resulting from step b)
- 15 d) mixing the impregnated metal oxide obtained from step c) with the zeolite of FER type.

37) The catalyst according to claim 33 containing phosphorous in a quantity ranging from 1 to 5 % wt with respect to the total weight of the catalyst.

38) A catalyst which comprises a metal of group VIII, a metal of group VI, a metal oxide as carrier and P in a quantity ranging from 0.1 to 10 % weight with respect to the total weight of the catalyst, prepared by

20

aqueous solution containing a soluble salt of the metal of group VI.

41) The catalyst according to claim 38, 39 or 40 containing phosphorous in a quantity ranging from 1 to 5 % wt with respect to the total weight of the catalyst.

42) The process according to claim 1 or 2 wherein the hydrocarbons boiling within the range of 35 to 250°C contain more than 1000 ppm of S.

43) The process according to claim 1 or 2 wherein hydrocarbons boiling within the range of 35 to 250°C derive from cracking processes.

44) The process according to claim 1 or 2 wherein the catalyst is in extruded form.

45) The process according to claim 31 carried out at a temperature ranging from 220 to 330°C.

EPO - DG 1

15. 08. 1998

PROCESS AND CATALYSTS FOR UPGRADING OF HYDROCARBONS  
BOILING IN THE NAPHTHA RANGE

Abstact

5       The present invention relates to the use of a  
catalytic system comprising a metal of group VIII, a  
metal of group VI, a metal oxide as carrier and suit-  
able quantities of a component selected from a zeolite  
of the FER type, phosphorous, and a mixture thereof, in  
upgrading of hydrocarbons boiling in the naphtha range  
10       containing sulfur impurities, namely in  
hydrodesulfurization with contemporaneous skeleton  
isomerization of olefins contained in said hydrocarbons  
and/or with reduction of olefins hydrogenation,  
carried out in a single step.

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Fig.1

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